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Determination of the crystal and magnetic structure of the $DyCrO_4$ -scheelite polymorph by neutron diffraction

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Abstract. Neutron diffraction data of $DyCrO_4$ oxide, prepared at 4 GPa and 833 K from the ambient pressure zircon-type, reveal that crystallize with the scheelite-type structure, space group $I4_1/a$. Accompanying this structural phase transition induced by pressure the magnetic properties change dramatically from ferromagnetism in the case of zircon to antiferromagnetism for the scheelite polymorph with a T_N = 19 K. The analysis of the neutron diffraction data obtained at 1.2 K has been used to determine the magnetic structure of this $DyCrO_4$-scheelite oxide which can be described with a k = [0, 0, 0] as propagation vector, where the Dy and Cr moments are lying in the *ab*-plane of the scheelite structure. The ordered magnetic moments are 10 μ_B and 1μ_B for Dy^{+3} and Cr^{+5} respectively.

1. Introduction

Phase transitions induced by pressure have been studied for the zircon mineral $ZrSiO_4$ and the analogous zircon-types of RXO_4 (X= As and V) which transform the tetragonal space group $I4_1/amd$ into a scheelite-type structure, space group $I4_1/a$. Recently for $YbPO_4$ and $LuPO_4$, it was revealed using in-situ synchrotron x-ray diffraction experiments that the pressure-induced zircon-to-scheelite transition is reversible and the scheelite high-pressure phase cannot be quenched to ambient conditions in these phosphates [1]. In the case of vanadates and arsenates, this phase transition from zircon to scheelite, with an increase in the density of 11%, takes place at 8 GPa and 773 K [2, 3]. Regarding the high pressure phase transformations in $RCrO_4$, in which we are interested, only few studies have been reported. This could be due to the high instability of Cr^{+5} and its tendency to be reduced to give the most stable distorted phase of perovskite $RCrO_3$. However, it has been recently reported by our research group that zircon-$RCrO_4$ phases transform to a scheelite polymorph at 4 GPa and 813 K for the $HoCrO_4$ and $TbCrO_4$ compounds, which are quenchable after releasing the pressure [4, 5]. Accompanying this structural phase transition from zircon to scheelite the magnetic properties change dramatically. In this sense, most of the zircon-type $RCrO_4$ oxides being ferromagnetic become antiferromagnetic for the corresponding known scheelite polymorph. Detailed structural analysis by x-ray diffraction

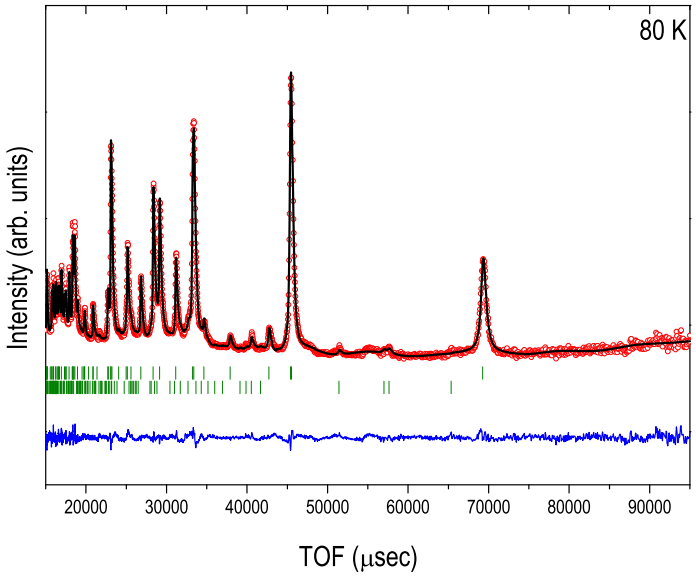

Figure 1. Rietveld refinement of the $DyCrO_4$ scheelite polymorph at 80 K for TOF neutron diffraction data. First raw of the vertical bars (i) corresponds to the $DyCrO_4$ scheelite. Second line (ii) is for $DyCrO_3$ distorted perovskite.

(XRD) and neutron diffraction (NPD) allow us to establish structure-magnetic properties relationships, which represents one of the main interests in the solid-state science. In this work, we aim to study the scheelite-$DyCrO_4$ oxide through investigating the structural and magnetic properties. Therefore, we focus first on the structural phase transition from the zircon-like to the scheelite-like structure under pressure and temperature. Second, we report the study of the magnetic properties of this $DyCrO_4$ from magnetization and neutron diffraction measurements.

2. Experimental

The $DyCrO_4$ zircon-phase sample, which was prepared by a precursor method described elsewhere, has been treated at 4 GPa and 833 K and 35-50 minutes in a CONAC-type press. $DyCrO_4$ scheelite oxide was first studied by X-ray powder diffraction using a Philips X'Celerator diffractometer with a primary beam monochromator consisting of a curved Ge (1 1 1) crystal aligned to obtain $CuK_{\alpha 1}$ radiation. A range of 2θ-angle between 10° and 90° was recorded with a step size of 0.0167° collected for 150s. Neutron diffraction experiments were done at the ISIS facility in the UK using the WISH cold-neutron time of flight (TOF) powder diffractometer. All obtained diffraction patterns were analyzed using the FullProf Suite Program. Magnetic susceptibility and magnetization measurements were performed in a Squid Quantum Design MPS XL from 300 K to 2 K temperature range in different magnetic fields up to 5T.

3. Results and discussion

3.1. Structural characterization

The structure of the $DyCrO_4$ compound obtained after treating the $DyCrO_4$-zircon polymorph at 4 GPa and 833 K has been refined from the X-ray and neutron diffraction data using the Rietveld method with the Fullprof program. As it is shown in Figure 1 the neutron diffraction data obtained at 80 K show the reflections conditions compatible with the space group $I4_1/a$ characteristic of the scheelite type structure.

The refined atomic positions are Dy at 4b (0, 1/4, 5/8), 4a (0, 1/4, 1/8) for Cr and the oxygen atoms are located at the 16f (x, y , z). The lattice parameters and main bond angles and interatomic distances are given in Table 1.

It is worth noting that small amount of impurities such as $DyCrO_3$ has also been include in the refinement, 8.98 (57) %. The zircon-type structure of $RCrO_4$ can be described as formed by

Table 1. Control sequences to describe lines and symbols in figure captions.

T (K)	80	1.2
a (Å)	5.0170(2)	5.0148(2)
b (Å)	11.3079(6)	11.3037(5)
V (Å^2)	284.62(2)	284.27(2)
U$_{Dy}$ (Å^2)	0.0003(8)	0.0002
U$_{Cr}$ (Å^2)	0.019(3)	0.0002
x$_o$	0.2437(5)	0.2437
y$_o$	0.6091(4)	0.6091
z$_o$	0.5486(2)	0.5486
U$_o$ (Å^2)	0.0105(14)	0.0002(8)
d$_{Cr-O}$ (Å)	1.7020(22) x 4	1.7020 x 4
d$_{Dy-O}$ (Å)	2.3413(22) x 4	2.3413 x 4
	2.4177(23) x 4	2.4177 x 4
Cr - O - Dy (deg.)	121.759 (114)	121.759
	132.242(82)	132.242
$\mu_{xy,Dy}$ (μ_B)	——	9.67(10)
$\mu_{xy,Cr}$ (μ_B)	——	0.99(12)
R$_B ragg$ (%)	2.44	5.49
R$_p$ (%)	3.81	4.02
R$_w p$ (%)	2.10	5.18
χ^2	2.62	1.32
Magnetic R-factor (%)	——	6.82

chains of CrO_4 and RO_8 polyhedra which are parallel to the c-axis and alternating by an edge sharing as seen in Figure 2a. Adjacent rods are connected along a and b-axis by zig-zag of edge sharing between RO_8 polyhedra. In case of the scheelite structure, CrO_4 distorted tetrahedra are aligned along the a-axis, while RO_8 bisdisphenoids are intercalated between the CrO_4 tetrahedra (Figure 2b).

The RO_8 polyhedra shares edges with adjacent RO_8 polyhedra and form along a-direction zig-zag chains, which are cross-linked by tetrahedra via corner-sharing (figure 2b). However, there is no edge-sharing between RO_8 and CrO_4 polyhedra. The difference in the tilting angle between different polyhedra, as well as in the packing after the transition provides an remarkable change in the Cr- O - R angles as it will be discussed later to explain the different magnetic behavior that presents this scheelite polymorph in comparison with the zircon one.

3.2. Magnetic properties

Figure 3 shows the evolution of the magnetic susceptibility with the temperature and it can observed that the susceptibility obeys a Curie- Weiss behavior, $\chi = C/T + \theta$ in the temperature range 300 - 40 K, see Figure 3 inset.

It is also observed a small anomaly at 150 K due to the presence of the distorted perovskite $DyCrO_3$ that become antiferromagnetically ordered at this temperature with a small canting. However the presence of this phase doesn't affect to the magnetic properties of the scheelite-$DyCrO_4$ oxide. In this sense, the obtained magnetic moment takes the value of 11.2 μ_B which fairly agrees with the expected for this compound is 10.80 μ_B. The Weiss constant (θ) takes

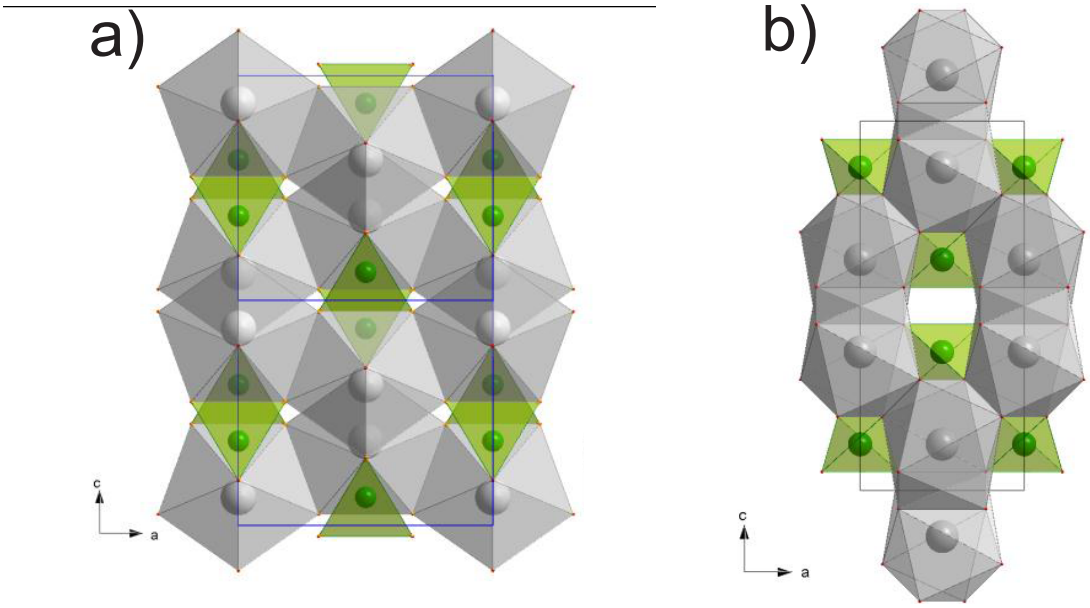

Figure 2. a) Crystal structure of the zircon-$DyCrO_4$ and b) scheelite-$DyCrO_4$ polymorph.

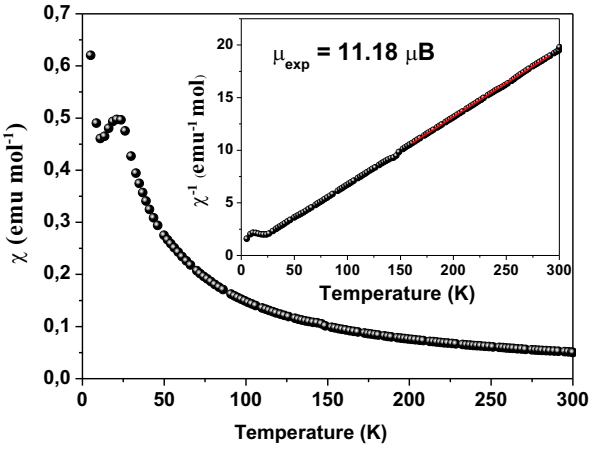

Figure 3. ZFC magnetization measurements for $DyCrO_4$ scheelite in a 0.05 T field. The inset shows the temperature dependence of the reciprocal susceptibility.

the value of -5.6 K which is indicative of the existence of antiferromagnetic interactions in this oxide. These interactions are fully confirmed the onset of a net maximum at 20 K in the χ vs T plot, see Figure 3. The increasing of the susceptibility below the T_N is due to presence of the small amount of impurities mentioned earlier. The different magnetic behavior that present both $DyCrO_4$ polymorphs, the scheelite form is antiferromagnetic, while the zircon-$DyCrO_4$ have been reported to be ferromagnetic [6] can be explained from the analysis of the structure of both polymorphs. As it was reported previously, these interactions take place through the superexchange Cr^{+5}-O-Dy^{+3} pathway in which both Cr and Dy are involved. Since the Cr-O and Dy-O interatomic distances remain almost constant for both polymorph, the change in the sign of the exchange integral going from the zircon to scheelite form is mainly due to remarkable differences found in the Cr^{+5}-O-Dy^{+3} bond angle found in both polymorphic phases. The magnetic structure of the $DyCrO_4$-scheelite polymorph has been determined from the analysis of the neutron diffraction data obtained at 1.2 K. The neutron powder diffraction patterns

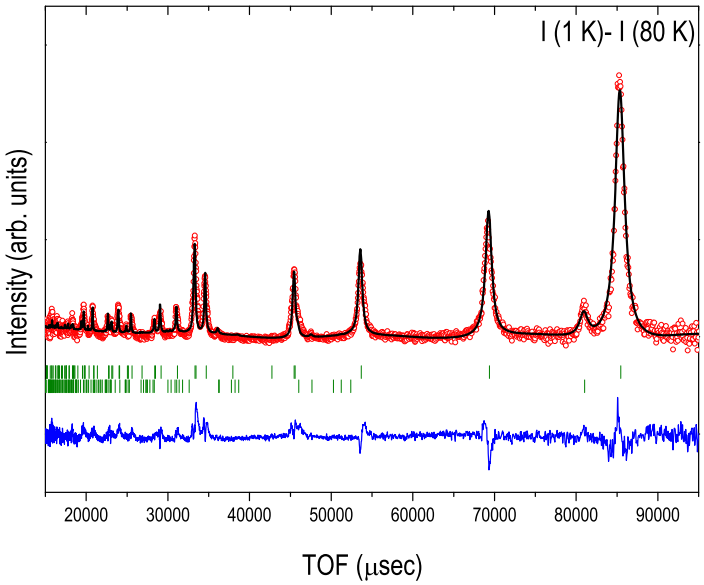

Figure 4. Magnetic structure fit from the difference between the 1.2 and 80 K neutron diffraction profiles of $DyCrO_4$. First ticks of vertical marks (i) corresponds to the magnetic contribution from the $DyCrO_4$ scheelite and second line (ii), magnetic contribution from the $DyCrO_3$ distorted perovskite.

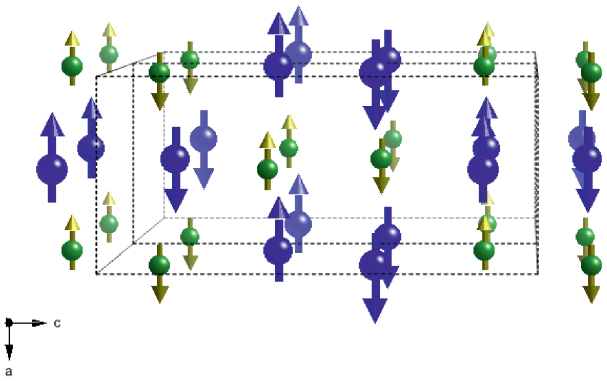

Figure 5. Magnetic structure of the $DyCrO_4$ scheelite. Blue and yellow arrows stem for the Dy and Cr magnetic moments respectively.

show the onset of new reflections forbidden for the space group $I4_1/a$ along with a progressive increase of certain reflections below $T_N = 20$ K. These magnetic reflections, see Figure 4, have been indexed on the basis of the coincidence between the crystal and magnetic cells, with the propagation vector k = [0, 0, 0].

The thermal evolution of the integrated intensity of the (002) and (110) magnetic reflections reveals that these magnetic reflections disappear at 22 K, a higher ordering temperature than the observed one from the magnetic susceptibility measurements. The magnetic structure is defined in the primitive P1 space group and the best agreement (RM= 0.068) between the experimental and calculated neutron diffraction profiles was obtained when Cr^{+5} and Dy^{+3} magnetic moments are aligned parallel to the ab-plane in the same manner like for $GdCrO_4$ scheelite [7],see Figure 5.

The saturation magnetic moments obtained from the Rietveld refinement are $9.67(10)\mu_B$ and $0.99(12)\mu_B$ for Dy^{+3} and Cr^{+5} respectively. As it can be observed in Figure 5 the magnetic moments of Dy^{+3} are antiferromagnetically coupled between the (Dy_2O_{14}) dimers resulting from the two (DyO_8) bisdiphenoids sharing a edge in the ab-plane of the scheelite structure. The Cr^{+5} moments are also antiferomagnetically coupled in the ab-plane of the structure given as

result the collinear magnetic structure depicted in Figure 5.

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